

SPECIFICATION
POLYPROPYLENE-BASED RESIN COMPOSITION
EXCELLENT IN MOLDABILITY AND PROPERTIES

FIELD OF THE INVENTION

This invention relates to a polypropylene-based resin composition comprising a propylene/ethylene block copolymer, ethylene/octene and/or ethylene/butene copolymer, styrene-based hydrogenated block copolymer rubber, and talc, good in injection moldability, flexural modulus of elasticity, resistance to impact and tensile elongation, excellent in internal molding pressure characteristics during the molding process, and suitable for injection-molded articles, e.g., automobile exteriors.

BACKGROUND OF THE INVENTION

It is widely known that polypropylene-based resin composition, comprising a polypropylene resin incorporated with an ethylene-based thermoplastic elastomer component (e.g., ethylene/propylene or ethylene/butene copolymer) and inorganic filler (e.g., talc), has been going into automobile parts. Various polypropylene resins, rubber components and inorganic fillers have been investigated and proposed, in order to improve moldability, mechanical properties and outer appearances of the polypropylene-based resin compositions.

Automobile parts are demanded to be produced by high-cycle molding and to be thinner articles, and require the materials of higher melting flow and rigidity. Some of the attempts to improve these properties have led to development of the compositions disclosed by Japanese Patent Laid-Open Nos.53843/1995 and 20684/1996. However, materials of still higher melting flow are required for the articles to be produced by high-cycle molding at low pressure, and the above compositions are still insufficient in melting flow to meet the above requirements.

Japanese Patent Laid-Open Nos.324725/1998, 29688/1999 and 43565/1999

MFR of 210 to 400g/10min. and isotactic pentad fraction (P) of 0.98 or more, and its copolymer portion containing propylene at 65 to 85% by weight; 50 to 70% by weight

Component (B): Ethylene/octene and/or ethylene/butene random copolymer, containing the comonomers at 28% by weight or more for the copolymerization and having an MFR of 0.5 to 20g/10min.; 10 to 25% by weight

Component (C): Styrene-based hydrogenated block copolymer rubber having the following structure, containing the segment A of polystyrene structure at 1 to 25% by weight; 4 to 9% by weight

A-B, or

A-B-A

wherein, the segment A is a polystyrene structure and segment B is an ethylene/butene or ethylene/propylene structure.

Component (D): Talc, having an average particle size of 10 μ m or less, determined by the laser-aided diffractometry; 16 to 24% by weight

The second invention is the polypropylene-based resin composition of the first invention whose resin composition has the following properties; internal molding pressure: 38MPa or less, MFR: 36 to 50g/10min., flexural modulus of elasticity: 1750MPa or more, brittleness temperature: -15°C or lower, tensile elongation: 200% or more, and difference between molding shrinkage and shrinkage after heating: 1.5/1000 or less.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention provides the polypropylene-based resin composition, comprising (A) propylene/ethylene block copolymer, (B) ethylene/octene and/or ethylene/butene random copolymer, (C) styrene-based hydrogenated block copolymer rubber, and (D) talc. Each of these components is described in more detail.

[I] Components of the resin composition

Isotactic pentad fraction (P) means the isotactic fraction of the pentad unit in the polypropylene molecular chain, determined by ^{13}C -NMR.

The copolymer portion of the propylene/ethylene block copolymer contains propylene at 65 to 85% by weight, preferably 67 to 75%. The propylene/ethylene block copolymer tends to have an insufficient tensile elongation when the propylene content is less than 65% by weight, and insufficient flexural modulus of elasticity when it is more than 85% by weight, and hence is undesirable.

(2) Production of the propylene/ethylene block copolymer

The propylene/ethylene block copolymer is produced in the presence of a catalyst of high stereoregularity. The examples of such catalysts include those produced by combining a titanium trichloride composition with an organoaluminum compound and aromatic carboxylate ester, where the titanium trichloride composition is produced by reducing titanium tetrachloride with an organoaluminum compound and treating the product with various electron donors and acceptors, as disclosed by Japanese Patent Laid-Open Nos.100806/1981, 120712/1981 and 104907/1983; and the impregnated type catalysts produced by bringing a magnesium halide into contact with an titanium tetrachloride and various electron donors, as disclosed by Japanese Patent Laid-Open Nos.63310/1982, 43915/1988 and 83116/1988.

The propylene/ethylene block copolymer is produced by copolymerization of propylene and ethylene in the presence of the above catalyst by a known method, e.g., vapor-phase fluidized bed, solution or slurry method.

(3) Content of the propylene/ethylene block copolymer

The above propylene/ethylene block copolymer is incorporated in the polypropylene-based resin composition of the present invention at 50 to 70% by

magnesium complex (e.g., alkyl aluminum-magnesium or alkyl alkoxyaluminum-magnesium complex) and alkyl aluminum or alkyl aluminum chloride, or a metallocene catalyst disclosed by, e.g., WO-91/04257. In particular, the metallocene catalyst gives the copolymer having more preferable effects. It can be produced by a known polymerization method, e.g., vapor-phase fluidized bed, solution or slurry method.

(3) Content of the ethylene/octene and/or ethylene/butene random copolymer

(C) Styrene-based hydrogenated block copolymer rubber (Component (C))

The styrene-based hydrogenated block copolymer rubber (Component (C)) as the constituent of the polypropylene-based resin composition of the present invention is the elastomer component used to make the above-described component (B) exhibit the effect of improving impact resistance more effectively, even in a small quantity.

A-B, or

wherein, the segment A is a polystyrene structure and segment B is an ethylene/butene or ethylene/propylene structure.

The concrete examples of the above-described styrene-based hydrogenated block copolymer rubber include styrene/ethylene/butene/styrene block copolymer (SEBS) and styrene/ethylene/propylene/styrene block copolymer (SEPS).

The elastomer copolymer of the above block structure may be a mixture of the tri-block and di-block structures, described above.

Ratio of the segment A of the above-described polystyrene structure is 1 to 25% by weight, preferably 5 to 25%, more preferably 7 to 22%. The copolymer rubber will have insufficient brittleness temperature, when the ratio is more than 25% by weight, and is undesirable.

(2) Production of the styrene-based hydrogenated block copolymer rubber

The styrene-based hydrogenated block copolymer rubber as the component (C) may be produced by the common anion living polymerization, where styrene, butadiene and styrene are polymerized consecutively to produce the tri-block structure which is then hydrogenated (production of SEBS), or the di-block copolymer of styrene and butadiene is produced first, and then converted into the tri-block structure by the aid of a coupling agent and hydrogenated styrene/isoprene/styrene tri-block copolymer may be produced by replacing butadiene with isoprene (production of SEPS).

(3) Content of the styrene-based hydrogenated block copolymer rubber

The elastomer of the above structure as the component (C) is incorporated in the polypropylene-based resin composition of the present invention at 4 to 9% by weight, preferably 5 to 8%, more preferably 5 to 7%.

The polypropylene-based resin composition will have insufficient brittleness properties when the content is less than 4% by weight, and an insufficient flexural modulus of elasticity and excessive Δ shrinkage when it is more than 9% by weight, and hence is undesirable.

(D) Talc (Component (D))

(1) Properties of talc

Talc (Component (D)) as the constituent of the polypropylene-based resin composition of the present invention has an average particle size of 10 μ m or less, preferably 0.5 to 8 μ m or less. The polypropylene-based resin composition has an insufficient flexural modulus of elasticity when the size is out of the above range, and hence is undesirable.

The average particle size can be determined from the cumulative particle size distribution curve at cumulative 50% by weight, the curve being prepared by a laser-aided diffraction analyzer (e.g., HORIBA's LA-920) or liquid layer settling type light transmission analyzer (e.g., SHIMADZU's CP). The average particle size was determined by the former method for the present invention.

The talc can be obtained by finely crushing naturally occurring one by a mechanical means, and classifying the particles precisely. The crushed particles may be classified first roughly and then more precisely.

The mechanical means include crushers, e.g., jaw, hammer, roll and jet crushers, and mills, e.g., screen, colloid, roll and vibration mills.

The crushed talc particles are classified by the wet or dry method once or repeatedly to have a desirable average size for the present invention. The useful devices for classifying them include cyclone, cyclone air separator, micro separator, and sharp-cut separator. It is preferable to crush the talc to have a size in a specific range, and classify the crushed particles by a sharp-cut separator, to prepare the talc for the present invention.

The talc may be surface-treated with various additives to improve its adhesion to or dispersibility in the polymer. These additives include a coupling agent of

organic titanate, coupling agent of organic silane, graft-modified polyolefin of unsaturated carboxylic acid or its anhydride, fatty acid, metallic salt of fatty acid, and fatty acid ester.

(2) Content of talc

It is important that the talc is incorporated in the polypropylene-based resin composition of the present invention at 16 to 24% by weight, preferably 19 to 22%.

The polypropylene-based resin composition will have an insufficient flexural modulus of elasticity when the content is less than 16% by weight, and an insufficient brittleness temperature when it is more than 24% by weight.

(E) Additional components (optional)

The polypropylene-based resin composition of the present invention may be incorporated with, in addition to the above essential components (A) to (D), one or more additional components (optional components), so long as the effect of the present invention is not notably damaged.

These additional components (optional components) useful for the present invention include antioxidant, e.g., phenol- and phosphorus-based ones; weathering-inhibiting agent, e.g., hindered amine-, benzophenone- and benzotriazole-based ones; nucleating agent, e.g., organoaluminum and organophosphorus compounds; dispersant represented by a metallic salt of stearic acid; colorant, e.g., quinacridon, perylene, phthalocyanine, titanium oxide and carbon black; whiskers, e.g., those of fibrous potassium titanate, fibrous magnesium oxysulfate, fibrous aluminum borate and calcium carbonate; and carbon fibers and glass fibers.

[II] Method of producing polypropylene-based resin composition

(1) Kneading

Table 1

ic peroxide

(2) Ethylene/octene and/or ethylene/butene random copolymer (Component (B))

Table 2 shows the elastomer components (Component (B)) used for the present invention.

Table 2

Elastomer components (Component (B))			
Types	MFR (g/10min.)	Comonomer content (wt.%)	Comonomer type
Elastomer-1	1.9	4.1	1-octene
Elastomer-2	2.1	4.5	1-octene
Elastomer-3	1	3.1	1-butene
Elastomer-4	0.8	3.2	1-butene
Elastomer-5	2.1	1.9	1-butene
Elastomer-6	5.9	3.9	1-octene

clamping force of 170 tons using a box-shaped mold with an embedded piezoelectric cavity pressure sensor, to measure the peak cavity pressure (internal molding pressure) during the filling process in the vicinity of the gate. The results are given in Tables 7 and 8.

	PP(A)		Elastomer component (B)		Elastomer component (C)		Talc (D)	
	Types	wt. %	Types	wt. %	Types	wt. %	Types	wt. %
EXAMPLE 1	PP-1	57	Elastomer-1	16	Styrene-1	7	Talc-1	20
EXAMPLE 2	PP-1	53	Elastomer-1	20	Styrene-1	7	Talc-1	20
EXAMPLE 3	PP-1	61	Elastomer-1	12	Styrene-1	7	Talc-1	20
EXAMPLE 4	PP-1	57	Elastomer-1	16	Styrene-1	8.5	Talc-1	18.5
EXAMPLE 5	PP-1	54	Elastomer-1	16	Styrene-1	7	Talc-1	23
EXAMPLE 6	PP-1	59	Elastomer-1	16	Styrene-1	7	Talc-1	18
EXAMPLE 7	PP-2	57	Elastomer-1	16	Styrene-2	7	Talc-1	20
EXAMPLE 8	PP-1	57	Elastomer-2	16	Styrene-2	7	Talc-1	20
EXAMPLE 9	PP-1	57	Elastomer-3	16	Styrene-1	7	Talc-1	20
EXAMPLE 10	PP-1	59	Elastomer-4	14	Styrene-1	7	Talc-1	20
EXAMPLE 11	PP-1	57	Elastomer-1	16	Styrene-2	7	Talc-1	20
EXAMPLE 12	PP-1	57	Elastomer-1	16	Styrene-3	7	Talc-1	20

Table 6

	PP(A)		Elastomer component (B)		Elastomer component (C)		Talc (D)	
	Types	wt. %	Types	wt. %	Types	wt. %	Types	wt. %
COMPARATIVE EXAMPLE 1	PP-1	8 0	Elastomer-1	1 0	Styrene-1	3	Talc-1	7
COMPARATIVE EXAMPLE 2	PP-1	4 0	Elastomer-1	3 0	Styrene-1	1 2	Talc-1	1 8
COMPARATIVE EXAMPLE 3	PP-1	5 1	Elastomer-1	1 4	Styrene-1	5	Talc-1	3 0
COMPARATIVE EXAMPLE 4	PP-3	5 7	Elastomer-1	1 6	Styrene-1	7	Talc-1	2 0
COMPARATIVE EXAMPLE 5	PP-4	5 7	Elastomer-1	1 6	Styrene-1	7	Talc-1	2 0
COMPARATIVE EXAMPLE 6	PP-5	5 7	Elastomer-1	1 6	Styrene-1	7	Talc-1	2 0
COMPARATIVE EXAMPLE 7	PP-6	5 3	Elastomer-1	2 0	Styrene-3	7	Talc-1	2 0
COMPARATIVE EXAMPLE 8	PP-1	5 7	Elastomer-5	1 6	Styrene-1	7	Talc-1	2 0
COMPARATIVE EXAMPLE 9	PP-1	5 7	Elastomer-6	1 6	Styrene-1	7	Talc-1	2 0
COMPARATIVE EXAMPLE 10	PP-1	5 7	Elastomer-1	1 6	Styrene-4	7	Talc-1	2 0
COMPARATIVE EXAMPLE 11	PP-1	5 3	Elastomer-1	2 0	Styrene-1	7	Talc-2	2 0
COMPARATIVE EXAMPLE 12	PP-1	6 0	Elastomer-1	2	Styrene-2	1 8	Talc-1	2 0
COMPARATIVE EXAMPLE 13	PP-7	5 7	Elastomer-1	1 6	Styrene-2	7	Talc-1	2 0
COMPARATIVE EXAMPLE 14	PP-8	5 7	Elastomer-1	1 6	Styrene-1	7	Talc-1	2 0

Table 7

	Properties					
	MFR (g/10min.)	Flexural modulus of easticity (MPa)	Brittleness temperature (°C)	Tensile elongation (%)	Internal molding pressure (MPa)	Δ shrinkage
EXAMPLE 1	41	2250	-25	250	36	○
EXAMPLE 2	36	2030	-30 \geq	380	37	○
EXAMPLE 3	50	2450	-16	209	35	○
EXAMPLE 4	38	2110	-30 \geq	250	36	○
EXAMPLE 5	41	2400	-24	230	37	○
EXAMPLE 6	42	2130	-23	270	35	○
EXAMPLE 7	48	2270	-22	260	34	○
EXAMPLE 8	41	2160	-28	250	36	○
EXAMPLE 9	37	2280	-18	400 \leq	35	○
EXAMPLE 10	37	2300	-17	390	36	○
EXAMPLE 11	39	2260	-26	350	36	○
EXAMPLE 12	38	2230	-27	250	36	○

Table 8

	Properties					
	MFR (g/10min.)	Flexural modulus of elasticity (MPa)	Brittleness temperature (°C)	Tensile elongation (%)	Internal molding pressure (MPa)	Δ shrinkage
COMPARATIVE EXAMPLE 1	65	1670	0 ≤	20	33	×
COMPARATIVE EXAMPLE 2	18	1270	-30 ≥	400 ≤	41	○
COMPARATIVE EXAMPLE 3	37	2700	-2	30	37	○
COMPARATIVE EXAMPLE 4	40	2270	-27	100	35	○
COMPARATIVE EXAMPLE 5	43	2200	-25	300	39	○
COMPARATIVE EXAMPLE 6	28	2160	-25	400 ≤	39	○
COMPARATIVE EXAMPLE 7	35	1760	-30 ≥	400 ≤	37	○
COMPARATIVE EXAMPLE 8	42	2350	-8	400 ≤	36	○
COMPARATIVE EXAMPLE 9	69	2140	-13	150	34	○
COMPARATIVE EXAMPLE 10	36	2250	-9	180	37	○
COMPARATIVE EXAMPLE 11	41	1620	-28	350	36	○
COMPARATIVE EXAMPLE 12	47	1960	-30 ≥	130	38	×
COMPARATIVE EXAMPLE 13	57	2260	-3	15	34	○
COMPARATIVE EXAMPLE 14	42	2200	-26	350	42	○

INDUSTRIAL APPLICABILITY

The polypropylene resin composition of the present invention is high in melting flow, exhibiting good properties and excellent in internal molding pressure, and hence can be molded into various types of articles, in particular automobile exteriors, e.g., bumpers, rocker moldings, sidemoldings and overfenders.